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1991 J. Phys.: Condens. Matter 3 S357

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Angle-resolved photoemission studies of planar and stepped oxide surfaces

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Received 25 April 1991

Abstract. The effect of surface imperfections on the angle-resolved photoemission spectra of planar and stepped (100) surfaces of TiO_2 and SrTiO_3 have been measured. Normal emission data, analysed using the direct transition model, are compared with a calculated *ab initio* bulk band structure for the Γ - Δ -X direction of rutile TiO_2 and a published band structure calculation for the Γ - Δ -X direction of SrTiO_3 . Selection rules are used to identify the symmetry of bands and resolve the rather broad spectral features. There is a close correlation between theory and experiment. The results for the stepped surfaces are little different to the planar surface data.

1. Introduction

Angle-resolved photoemission (ARP) data from low-Miller-index surfaces have been extensively used in the determination of the electronic structure of clean metals and semiconductors within the direct transition model [1-3]. Relatively recently the same direct transition model has been extended to oxides in analysis of O 2p band results. This includes studies of SrTiO_3 [4], NiO [5] and CoO [6].

In this paper we test the use of the direct transition model in analysis of normal emission data from the (100) face of TiO_2 , which possesses a rather complex valence band structure relative to the oxides previously studied. In addition, we also compare spectra from planar and stepped $\text{TiO}_2(100)$ and $\text{SrTiO}_3(100)$. These latter experiments allow us to assess the influence of random steps, which may introduce extra features in the photoemission due to Umklapp, or other, processes [1] as seen on stepped metal surfaces [7]. Clearly such a comparison has far-reaching consequences for the use of ARP in the examination of the electronic structure of another group of stepped oxide samples, the new high- T_c materials [8].

In order to interpret our experimental data, we have calculated the band structure of rutile TiO_2 along the Γ - Δ -X direction using an *ab initio* method within the local density approximation [9].

In combination with published results [4], this paper demonstrates that normal emission ARP spectra from the surfaces of planar and stepped $\text{TiO}_2(100)$ and

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$\text{SrTiO}_3(100)$ can be successfully interpreted within the direct transition model. Photoemission data from the planar and stepped surfaces show only minor differences.

2. Experimental results

Angle-resolved photoemission experiments employed the toroidal grating monochromator ($17 \leq h\nu \leq 120 \text{ eV}$) and VG ADES 400 electron energy analyser on station 6.2 at the SRS, Daresbury Laboratory. The analyser angular acceptance was $\pm 2^\circ$ (FWHM), the combined (monochromator + analyser) energy resolution being $\leq 150 \text{ meV}$. All spectra were recorded at a substrate temperature of 150 K to reduce phonon broadening effects. The chamber base pressure during the experiment was $\sim 9 \times 10^{-11} \text{ mbar}$.

TiO_2 and SrTiO_3 single crystals were obtained in the form of boules (Commercial Crystals Laboratory). TiO_2 wafers ($10 \times 10 \times 2 \text{ mm}$) were used, one being cut and polished ($0.25 \mu\text{m}$) to within 0.1° of (100), the other being polished $2.6 \pm 0.1^\circ$ off the (100) plane towards [001]. The planar $\text{SrTiO}_3(100)$ wafer sample was cut and polished ($0.25 \mu\text{m}$) to within 0.1° of (100). Sample orientation was checked using Laue diffraction. The wafer samples were prepared as clean stoichiometric surfaces as detailed in [10]. Normal emission spectra were recorded in the range $22 \leq h\nu \leq 47 \text{ eV}$ at an angle of incidence with respect to the surface normal of 20° and 70° incidence for TiO_2 and 30° and 70° for SrTiO_3 . Changing the angle of incidence from lower to higher angles increases the E -vector component of the light perpendicular to the surface. This allows us to apply symmetry selection rules for photoemission [1].

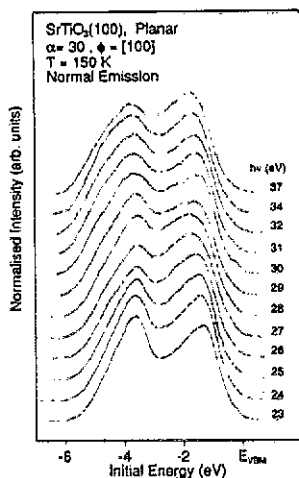


Figure 1. Normal emission spectra from planar $\text{SrTiO}_3(100)$ for photon energies between 23 to 37 eV, recorded at an incidence angle of 30° corresponding to near s polarization. All spectra were recorded at 150 K.

3. Results and discussion

Selected normal emission spectra for photon energies between 22–37 eV are shown for planar $\text{SrTiO}_3(100)$ and stepped $\text{TiO}_2(100)$ in figures 1 and 2, respectively. The corresponding spectra for stepped $\text{SrTiO}_3(100)$ are published elsewhere [4].

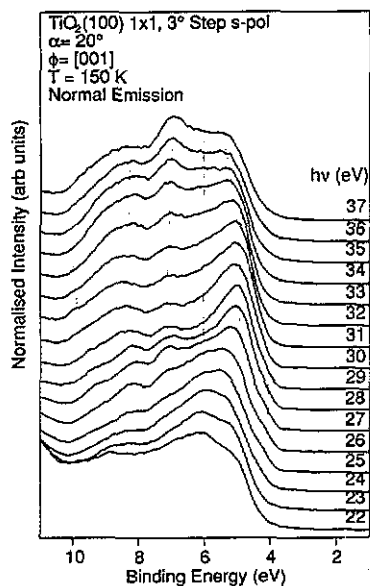


Figure 2. Normal emission spectra from planar $\text{TiO}_2(100)$ for photon energies between 22 and 37 eV, recorded at an incidence angle of 20° corresponding to near s polarization. All spectra were recorded at 150 K.

Spectra above 37 eV contain Ti 3p resonance effects [4] and cannot be reliably used in band-mapping. The (100) spectra show a number of broad, closely overlapping peaks. This arises from increased phonon broadening in oxides compared to metals [4] and to the complex nature of the bands, especially for TiO_2 . To obtain the dispersion relations along the Γ - Δ -X direction, we assume direct transitions into a free electron final state of form [1].

$$E(\text{eV}) = (\hbar^2 k_{\perp}^2 / 2m^*) - E_0. \quad (1)$$

In (1) k_{\perp} is the component of the wave-vector of the outgoing photoelectron normal to the surface, m^* is the effective mass of the electron and E_0 is the inner potential with respect to the Fermi energy. In the direct transition model spectral features originate from initial states along the Γ - Δ -X symmetry line in the simple cubic (SrTiO_3) and primitive tetragonal (TiO_2) Brillouin zones.

For the planar $\text{SrTiO}_3(100)$ normal emission spectra contained in figure 1, selection rules [11] indicate that only initial states of Δ_1 or Δ_5 symmetry should be observed. The binding energy scale of the spectra in figure 1 is referenced to the theoretical valence band maximum [4]. A comparison of the earlier stepped surface data [4] recorded in the same geometry at the same temperature reveal only slight differences. The most significant change is associated with the highest binding energy (BE) peak of Δ_5 symmetry. This is weaker and less well-resolved compared to the stepped surface data, contrary to our expectations. However, cleaved samples can display a noticeably sharper LEED pattern than wafer samples, possibly indicating that in some aspects the surface order is superior for the cleaved sample. Apart from this minor difference, the

number of peaks, their relative intensities and peak dispersions are essentially identical for the two cases. This shows that the effect of cleavage steps on the photoemission data is negligible for the $\text{SrTiO}_3(100)$ surface. A comparison of the direct transition model-derived empirical bands obtained from the stepped surface data with calculated bands has been presented in detail elsewhere [4]. Hence, only the major points will be presented here. A modified band structure due to Wolfram *et al* [12] gives the best comparison with the experimental Δ_1 and Δ_5 bands. To achieve better agreement with experiment the calculated initial state bands were adjusted by rigidly shifting the two highest BE bands by 1 eV to higher BE. This shift can be justified if it is assumed that the calculation underestimates both the ionic crystal field splitting and the mixing of Ti 3d orbitals in these two bands [4]. For both the planar and stepped surface there is no need to ascribe any of the experimental features to one-dimensional density of states (ODDOS). This in itself suggests that Umklapp-scattering associated with defects and steps, or phonon-assisted indirect scattering, is relatively weak.

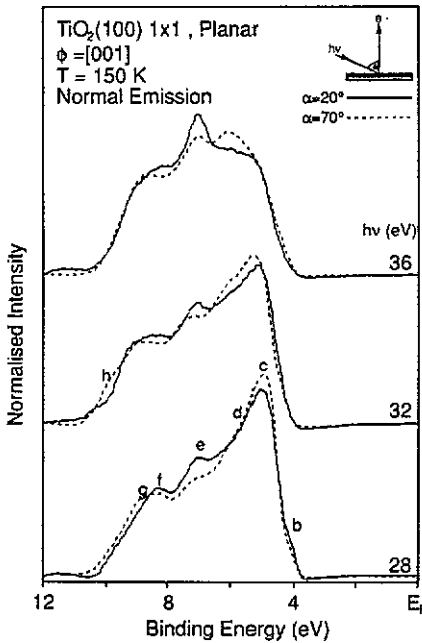


Figure 3. Normal emission spectra from planar $\text{TiO}_2(100)$ after background subtraction and normalization to the photon flux. Data were recorded at $h\nu = 28, 32$ and 36 eV and at an incidence angle of 20° and 70° . These angles correspond to near s and near p polarization.

Interpretation of the $\text{TiO}_2(100)$ data is strongly aided by the use of selection rules. Polarization effects are seen in figure 3, which contains normal emission data recorded at 20° and 70° incidence angles and $h\nu = 28, 32, 36$ eV. Careful inspection of the relative intensities within the valence band spectra and selection rules for direct transitions leads us to identify seven spectral features assigned b-h in figure 3. For the Δ line of the TiO_2 Brillouin zone the selection rules are complicated by the (100) surface possessing C_{2v} point group symmetry under the non-symmorphic D_{4h}^{14} space group. In this case a non-primitive translation vector, $\mathbf{p}(\gamma = \exp -i\pi p)$, is included in the irreducible representations of the point group [13]. In the direct transition

model it follows that the allowed-final-state changes as the final state crosses Brillouin zone boundaries in the extended zone scheme [13]. However, for the photon energy range used here and the value of E_0 employed in our analysis, it transpires that the only allowed final state is Δ_1 , and transitions are allowed from Δ_1 , Δ_2 and Δ_3 initial states when the E -vector is parallel to [100], [001] and [010], respectively [13]. Hence, in normal emission geometries no transitions should be seen from Δ_4 initial states.

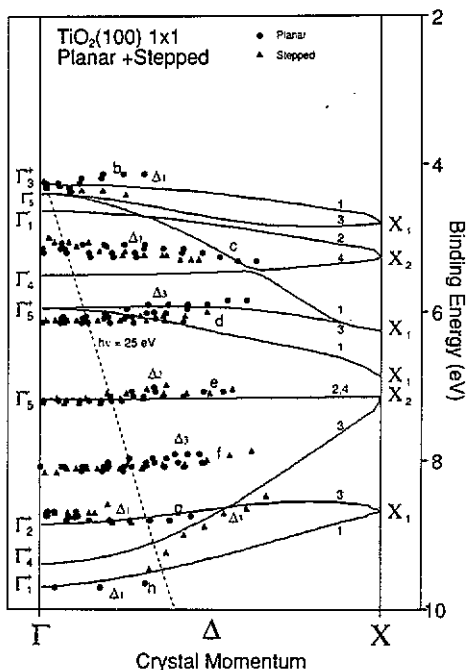


Figure 4. The empirical Δ -line band structure in the reduced zone scheme obtained from analysis of $22 \leq h\nu \leq 37$ eV ARP spectra from planar (circles) and stepped (triangles) $\text{TiO}_2(100)$. The solid curves are the calculated bulk band dispersions. The free-electron final state for $h\nu = 25$ eV, dropped by the photon energy, is shown as a dotted line.

The values of the inner potential and the effective electron mass were empirically adjusted to obtain initial state dispersions symmetric about Γ [14], the resulting values being $E_0 = -9$ eV and $m^* = 0.95 m$. The empirical band structure obtained from both the planar and vicinal surface data is shown in figure 4. In figure 4 it is compared with the results of our theoretical band structure, calculated within the local density approximation using a well tested *ab initio* atomic orbital-based method [9]. The peak positions in the spectra were obtained by subtracting an exponential background from the raw data and then fitting the resulting spectra with gaussian peaks. There is good agreement of the empirical Δ -line band widths and dispersions with the majority of our calculated bands after the calculated bands have been rigidly shifted 0.3 eV to lower BE. The agreement with other recent calculations [15,16] is also quite satisfactory. Only one flat experimental band at around 8 eV BE cannot be associated with a corresponding theoretical band. The position of this feature in comparison to theory, and its presence in both the planar and vicinal data, would also seem to rule out its explanation in terms of step-induced Umklapp. This feature will be discussed in

a forthcoming publication [13]. As can be seen in figure 4, there is little difference between the planar and stepped data except for the lowest Δ_3 band, which is not clearly discernible in the planar surface data. Moreover, although some of the bands in our data show little dispersion, we are not forced to invoke either phonon-assisted indirect transitions [1] or Umklapp processes [1] to explain their origin, as in the case of the SrTiO₃(100) data.

4. Summary

We have shown in this paper that the complex valence band exhibited by TiO₂(100) can be deduced from angle-resolved photoemission data. To do so we employ polarization selection rules and a conventional band mapping procedure, assuming primary cone emission and direct transitions into a free-electron-like final state. We have also shown that there are a few differences between the ARP data from planar and stepped surfaces. Those observed represent minor differences in peak widths and intensities. This differs slightly from the behaviour of planar and stepped metal surfaces [7]. For instance a comparison of Ni(111) and Ni(s)-[5 (111)*(110)] ARP results reveals the presence of an extra single sharp dispersionless peak in the latter data which has been attributed to the presence of steps.

Acknowledgments

This work was funded by the Science and Engineering Research Council, including the award of studentships to CAM and PJH.

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